

## CONTROLLED OXIDATION OF SILANE

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**Summary**—The study of  $\text{SiH}_4$ -oxidant systems was undertaken to gain insight into reaction mechanisms that could cause the formation of  $\text{SiO}_2$  in the gas phase or on the reactor wall, rather than on the surface of the silicon wafers to be coated.

A gas reactor system was designed and built to determine the relative stabilities of various  $\text{SiH}_4$ -oxidant combinations and to monitor the oxidation of  $\text{SiH}_4$  to  $\text{SiO}_2$  by observing the change in absorption of the  $925\text{ cm}^{-1}$  peak of the  $\text{SiH}_4$  spectrum. Stability, as defined by the initiation temperatures for the oxidation reaction, indicated that at silane concentration of 0.8% or less,  $\text{N}_2\text{O-SiH}_4\text{-N}_2$  mixtures begin to react from  $370$  to  $525^\circ\text{C}$  and  $\text{O}_2\text{-SiH}_4\text{-N}_2$  between  $140$  to  $270^\circ\text{C}$ .  $\text{CO}_2\text{-SiH}_4\text{-N}_2$  was stable to  $520^\circ\text{C}$ .

All of the above oxidant- $\text{SiH}_4\text{-N}_2$  combinations could be premixed at room temperature without reacting. In order to obtain kinetic data, the decay of  $\text{SiH}_4$  concentration as a function of temperature was obtained by determining the relationship between infrared transmittance and  $\text{SiH}_4$  concentration. From these data the apparent activation energies for the  $\text{SiH}_4\text{-O}_2$  and  $\text{SiH}_4\text{-N}_2\text{O}$  reactions were found to be 8 kcal and 32 kcal, respectively. Analysis of reaction products between  $240$  and  $450^\circ\text{C}$  indicated that hydrogen rather than water vapor was formed. The most probable reaction equation is  $\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2$ .

## INTRODUCTION

VAPOR deposition of  $\text{SiO}_2$  films by the thermal oxidation of  $\text{SiH}_4$  is widely used in the manufacture of solid-state devices and integrated circuits. It is used, for example, to deposit protective layers and electrical insulation,<sup>1</sup> as a means of adjusting capacitance, and as a diffusion source of dopants.<sup>2,3</sup> The normal deposition temperature is  $250$  to  $475^\circ\text{C}$ .<sup>4</sup>

<sup>1</sup> A. Mayer, et al, "Surface Passivation Techniques for Compound Solid-State Devices," Air Force Contract F33(657)-11615, Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio.

<sup>2</sup> A. W. Fisher, J. A. Amick, H. Hyman, and J. H. Scott, Jr., "Diffusion Characteristics and Applications of Doped Silicon Dioxide Layers Deposited from Silane ( $\text{SiH}_4$ )," *RCA Review*, Vol. 29, p. 533, Dec. 1968.

<sup>3</sup> J. A. Amick, and A. W. Fisher, "Isolation Techniques for Fabricating Integrated Circuits—I. Laminate Substrates," *RCA Review*, Vol. 29, p. 475, Dec. 1968.

<sup>4</sup> N. Goldsmith and W. Kern, "Deposition of Vitreous Silicon-Dioxide Films from Silane," *RCA Review*, Vol. 29, p. 153, March 1967.

A characteristic of the process is that the rate of  $\text{SiO}_2$  deposition is quite sensitive to changes in the  $\text{SiH}_4$  concentration and changes in the feed stream flow patterns within the reactor. This sensitivity is reflected in significant changes in the deposition rate.

In practice, the  $\text{SiH}_4$  oxidation reaction has been observed to occur in the gas phase and on all heated surfaces with the reactor. Depending on reactor design and flow conditions, a variable amount of  $\text{SiH}_4$  can be stripped from the feed stream and deposited on reactor walls. For this reason, operating conditions are adjusted so that  $\text{SiH}_4$  concentration is as dilute as possible consistent with a reasonable deposition rate (600 to 1500 Å per minute).

To incorporate controlled amounts of boric or phosphoric oxide in the deposit by the simultaneous oxidation of  $\text{PH}_3$  or  $\text{B}_2\text{H}_6$  with  $\text{SiH}_4$ , an insight into the oxidation mechanism is desirable. Close control of the doping process is made difficult by differences in the stability of the hydrides in oxygen. This can result in differences in the composition of the deposited layer depending upon the geometry of the reactor and the initiation temperature of the dopant species.

One method of obtaining better control over the  $\text{SiH}_4$ - $\text{SiO}_2$  deposition process would be to obtain a  $\text{SiH}_4$ -oxidant combination that would permit the temperature at which the reaction is initiated to be increased. This temperature is determined by the reaction kinetics rather than by the free energy of reaction, because the free energy of formation of  $\text{SiO}_2$  is so high, relative to practical oxidants, that the reaction should go to completion at room temperature. Thus, in the practical systems examined, which consist of  $\text{SiH}_4$  reacting with  $\text{O}_2$ ,  $\text{N}_2\text{O}$ , or  $\text{CO}_2$ , the free energy of reaction ranges from 190 to 94 kcal/mole.<sup>5</sup> The pronounced differences in initiation temperatures observed here as a function of specific reactants and their concentration levels indicate that the kinetics were affected perhaps by a change from a reaction-controlled mode to a diffusion-controlled mode. Similar considerations may then be applied to oxidation of  $\text{PH}_3$  and  $\text{B}_2\text{H}_6$ . An examination of the reaction of  $\text{SiH}_4$  with  $\text{O}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CO}_2$  was made and is described here.

#### APPARATUS

A method of monitoring the  $\text{SiH}_4$  concentration as a function of time and temperature was developed. A Beckman IR8 Spectrophoto-

<sup>5</sup> C. E. Wicks and F. E. Block, *Thermodynamic Properties of Elements, Their Oxides, Halides, Carbides, and Nitrides*, Bulletin 605, Bureau of Mines.

meter was used to determine the infrared spectrum of  $\text{SiH}_4$  (Figure 1). The spectrum indicated useable peaks in the  $2200\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  regions. The absorption spectra for some of the oxidants ( $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , etc.) and reaction products were found to be limited to the  $2200\text{ cm}^{-1}$  region, while the  $900\text{ cm}^{-1}$  region was occupied only by the  $\text{SiH}_4$  lines. The optics of the spectrophotometer, therefore, were aligned on the  $925\text{ cm}^{-1}$  absorption peak, and the variation in peak height as

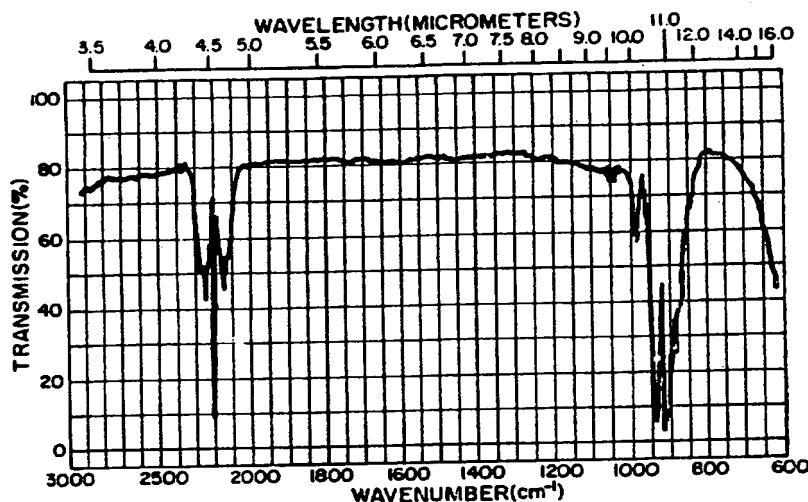


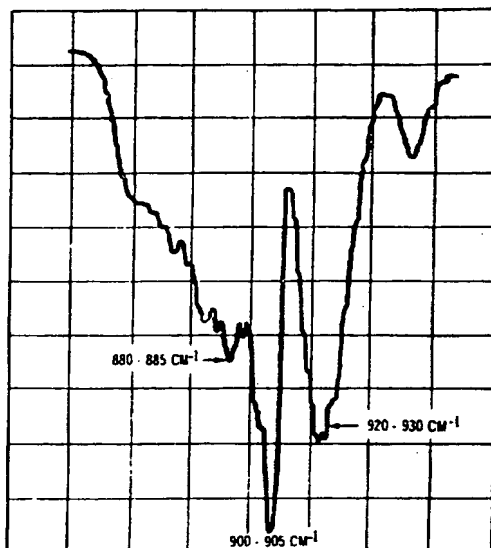
Fig. 1—Infrared spectrum of  $\text{SiH}_4$ .

percent transmission through a 10-cm gas cell was monitored. An expanded profile of this part of the infrared spectrum is shown in Figure 2.

The monitoring equipment was part of a simplified gas reactor system (Figure 3) consisting of

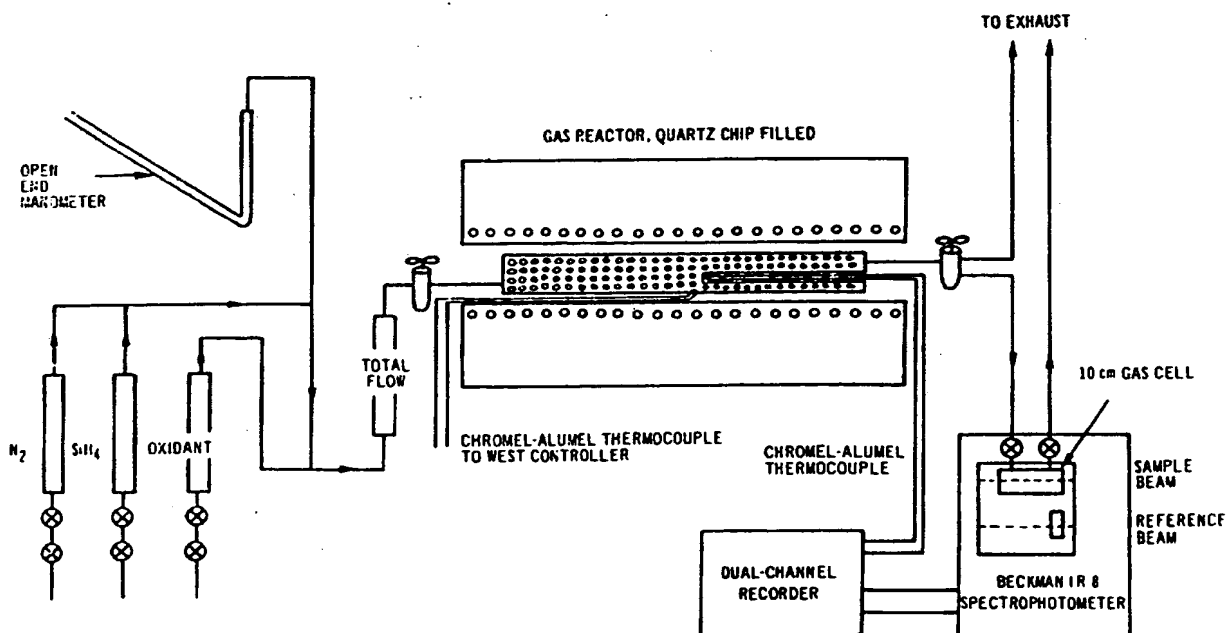
- (1) flow controls for  $\text{SiH}_4$ , oxidant, and nitrogen;
- (2) the gas reactor, filled with quartz chips, in a resistance-wound furnace;
- (3) a 10-cm gas cell mounted in a Beckman IR8 Spectrophotometer;
- (4) a dual-channel strip-chart recorder.

The combined gases were piped into the reactor and were exhausted through the 10-cm gas cell. The dc output of the spectrophotometer at  $925\text{ cm}^{-1}$  and the dc output of the chromel-alumel thermocouple inserted in a quartz tube within the reactor were recorded on a dual-channel strip-chart recorder. Thus,  $\text{SiH}_4$  concentration was monitored as a function of temperature and time.

PARTIAL SiH<sub>4</sub> SPECTRUMFig. 2—Partial SiH<sub>4</sub> spectrum.

## REACTION TEMPERATURES

The test procedure was to adjust the SiH<sub>4</sub> and N<sub>2</sub> gas streams to the required concentration within the reactor at room temperature. The 925 cm<sup>-1</sup> absorption peak was used to establish a base line on a strip-chart recorder for SiH<sub>4</sub> in N<sub>2</sub> at room temperature. Oxidant was

Fig. 3—Gas reactor system for SiH<sub>4</sub>-oxidant reaction.

then added. If no change occurred, the furnace was turned on and concentration and temperature rise were monitored as a function of time. The concentration range examined for most of the tests was 0.2 to 0.8%  $\text{SiH}_4$  and an oxidant/ $\text{SiH}_4$  ratio between approximately 2 and 20.

Test results indicated that at room temperature no reaction takes place between  $\text{SiH}_4$  (0.2-0.8%) and  $\text{O}_2$ ,  $\text{N}_2\text{O}$ , or  $\text{CO}_2$ . Table I gives the reaction initiation temperatures observed for the 0.2-0.4%  $\text{SiH}_4$  range.

Table I—Reaction Initiation Temperatures

Mixture	Reaction Initiation Temperature ( $^{\circ}\text{C}$ )	Conditions
$\text{SiH}_4 + \text{O}_2 + \text{N}_2$	140—270	0.2-0.4 $\text{SiH}_4$ , Oxidant/ $\text{SiH}_4$ = 2-20 at 0.4% $\text{SiH}_4$ .
$\text{SiH}_4 + \text{N}_2\text{O} + \text{N}_2$	370—540	0.2-0.4 $\text{SiH}_4$ , Oxidant/ $\text{SiH}_4$ = 2-20 at 0.4% $\text{SiH}_4$ .
$\text{SiH}_4 + \text{CO}_2 + \text{N}_2$	520	0.2% $\text{SiH}_4$ , Oxidant/ $\text{SiH}_4$ $\approx$ 5

Thus, contrary to prediction,  $\text{SiH}_4\text{-O}_2\text{-N}_2$ ,  $\text{SiH}_4\text{-N}_2\text{O-N}_2$ , and  $\text{SiH}_4\text{-CO}_2\text{-N}_2$  mixtures are stable up to at least 0.8%  $\text{SiH}_4$  at room temperature. This was found to be the case whether the gases were transported in Pyrex, copper, or stainless-steel lines.

#### MEASUREMENT OF SILANE CONCENTRATION

To examine the kinetics of the oxidation of  $\text{SiH}_4$  for different  $\text{SiH}_4$ -oxidant combinations, it was necessary to determine the relationship between infrared transmittance and  $\text{SiH}_4$  concentration. Mass-spectrometer analysis of  $\text{SiH}_4$  samples were taken over a concentration range of from 0.05 to 0.75%, which corresponds to a transmittance range of from 80 to 15% in the 10-cm cell. These data, plotted in Figure 4, indicate that the relationship between the  $\text{SiH}_4$  concentration and  $\log 1/T$  generally approximates the prediction of linearity from Beer's Law:

$$\log \frac{I_0}{I} = \log \frac{1}{T} = K \cdot C_{\text{SiH}_4}$$

where  $I_0$  = intensity of incident beam

$I$  = intensity of emerging beam

$T$  = transmittance

$K$  = constant (absorptivity, cell length)

$C_{\text{SiH}_4}$  = molar concentration of  $\text{SiH}_4$

## REACTION KINETICS

A thermal arrest technique (temperature and concentration held constant) was used to obtain each datum point, and the reaction of  $\text{SiH}_4$  with  $\text{O}_2$  and  $\text{N}_2\text{O}$  were compared. The decay of a 0.4%  $\text{SiH}_4$  concentration at an oxidant/ $\text{SiH}_4$  ratio of 7 was monitored. The data, shown in Figure 5, are consistent with previous data in that the initiation temperature for the  $\text{SiH}_4$ - $\text{N}_2\text{O}$  reaction is significantly higher than for the  $\text{SiH}_4$ - $\text{O}_2$  reaction.

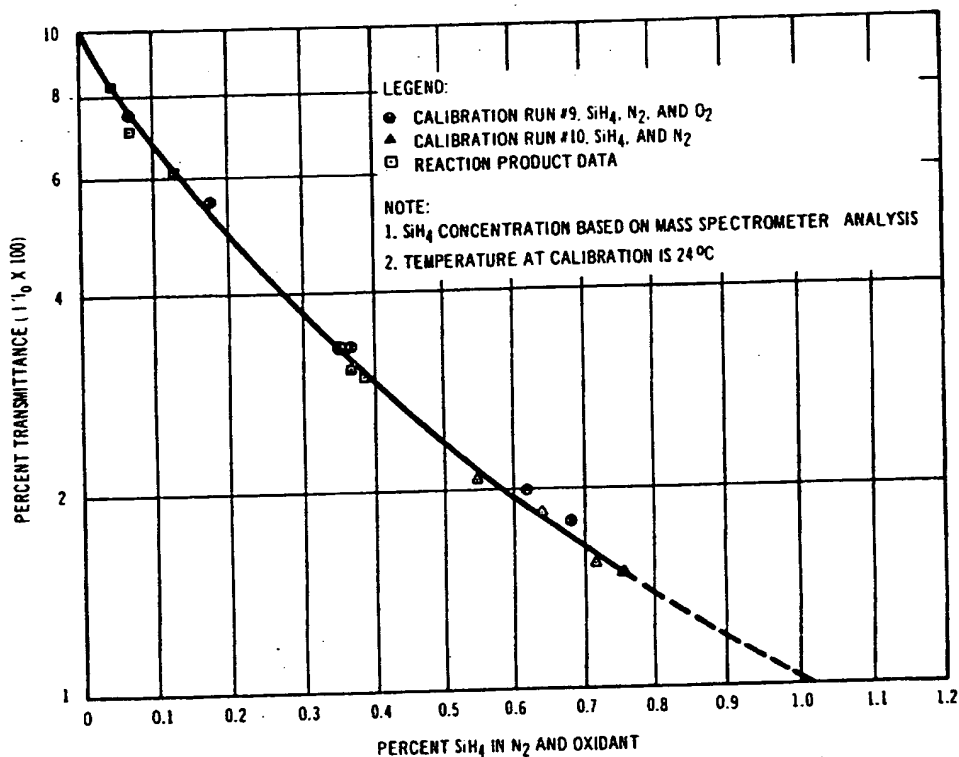
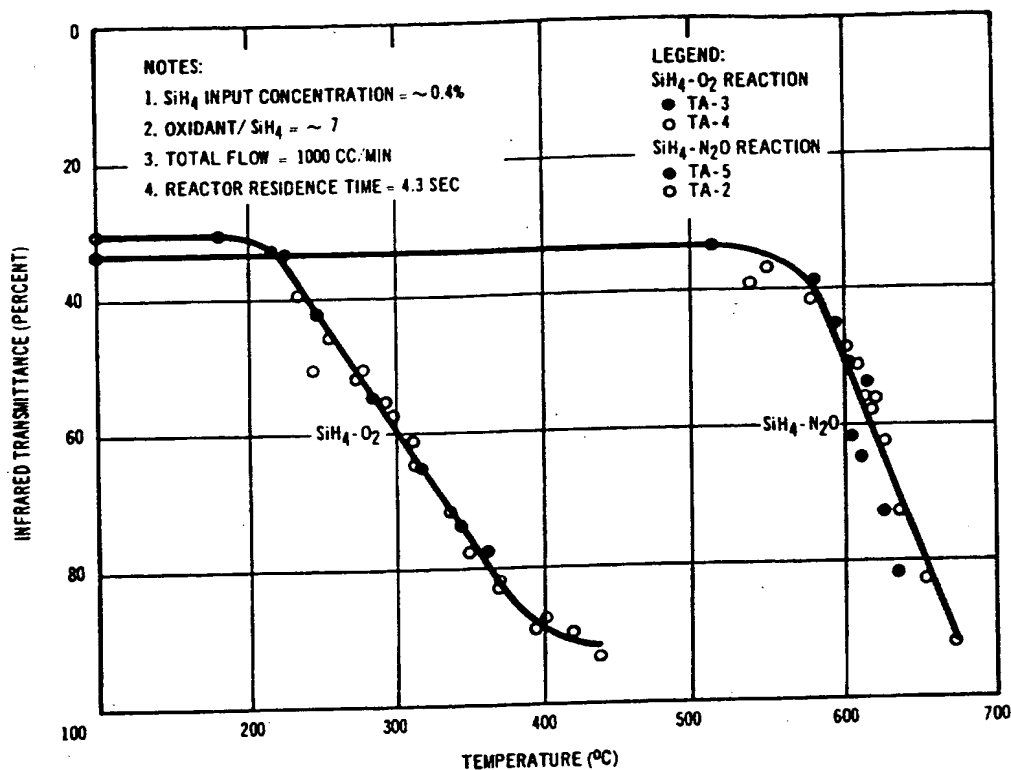
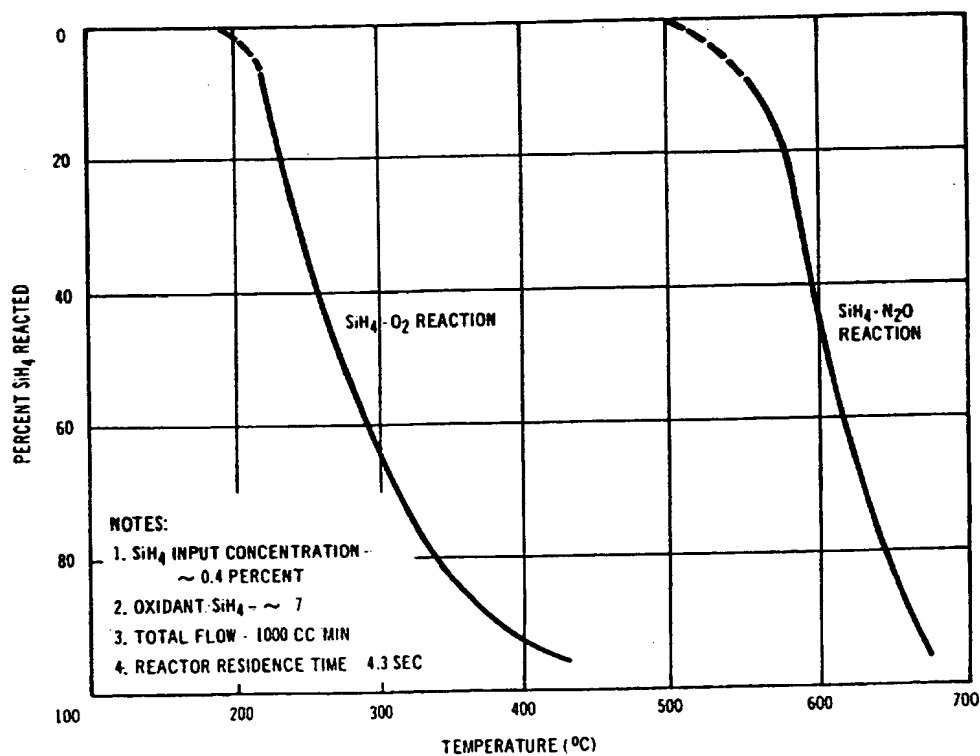


Fig. 4— $\text{SiH}_4$  concentration versus infrared transmittance of the 920 to 930  $\text{cm}^{-1}$  ( $10.8 \mu\text{m}$ ) peak.

With a calibration curve (IR transmittance versus  $\text{SiH}_4$  concentration), the transmittance data was converted to percent  $\text{SiH}_4$  reacted as a function of gas temperature. This curve is shown in Figure 6.

The concentration versus temperature curves shown in Figure 6 are not linear, however, and can not be accurately extrapolated to the initial reaction temperature. Since it is difficult to quantitatively compare the two oxidation reactions, a theoretical basis for determining an "apparent activation energy" was considered.

The reaction is bimolecular and would normally be described by a second-order kinetic expression. However, since the oxidant con-

Fig. 5—Infrared monitoring of oxidation of  $\text{SiH}_4$ .Fig. 6—Reaction of  $\text{SiH}_4$  with  $\text{O}_2$  and  $\text{N}_2\text{O}$ .

centration is high relative to the amount that reacts, the reaction rate would appear to be predominantly a function of  $\text{SiH}_4$  concentration rather than both  $\text{SiH}_4$  and oxidant concentrations. Therefore, a unimolecular reaction might describe the reaction kinetics better than a bimolecular reaction.

In the tests plotted in Figure 5, a uniform gas-temperature profile was obtained within the reactor by holding the total gas-flow rate constant ( $1000 \text{ cm}^3/\text{min}$ ) for all tests. This resulted in a calculated reaction or residence time of 4.3 seconds. However, since kinetic data are usually obtained by monitoring a concentration change as a function of time rather than temperature, an unconventional manipulation of the kinetic expressions was required.

For a first-order reaction, the relationships between concentration, time, and temperature<sup>6</sup> are:

$$-\frac{dC_{\text{SiH}_4}}{dt} = kC_{\text{SiH}_4} \quad (1)$$

$$k = k_o \exp \left\{ -\frac{\Delta E_A}{RT} \right\} \quad (2)$$

By integrating and combining these equations, an expression is derived that relates a change in reactant concentration and gas temperature to an activation energy:

$$\ln \left( t^{-1} \ln \frac{C_o}{C} \right) = \frac{-\Delta E_A}{RT} + \ln k_o \quad (3)$$

where  $C_o$  = input concentration,

$C$  = exhaust concentration,

$t$  = reaction time,

$E_A$  = apparent activation energy,

$T$  = gas temperature,

$k$  = absolute reaction rate,

$k_o$  = frequency factor.

From the data in Figure 6, where between 20 and 80%  $\text{SiH}_4$  reacted, the reaction rate of  $\ln(t^{-1} \ln C_o/C)$  was calculated and plotted against

<sup>6</sup> A. A. Forst and R. G. Pearson, *Kinetics and Mechanism*, 2nd ed., John Wiley and Sons, Inc., New York (1961).



reciprocal temperature. The resulting curves, Figures 7 and 8, are straight-line functions, indicating that the oxidation of  $\text{SiH}_4$  at the stated concentration levels can be considered a monomolecular reaction. The apparent activation energies calculated from the slopes of these curves are

$\text{SiH}_4\text{-O}_2$  reaction = 8 kcal

$\text{SiH}_4\text{-N}_2\text{O}$  reaction = 32 kcal

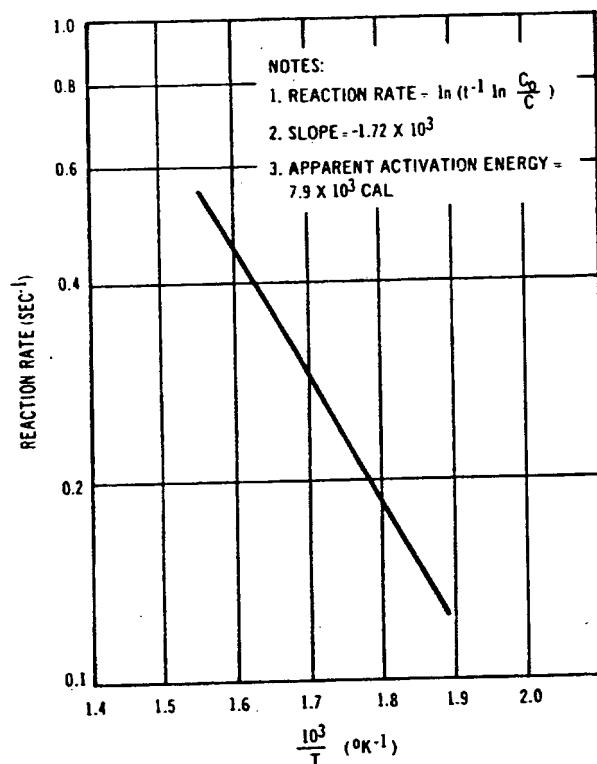


Fig. 7—Temperature dependence of the  $\text{SiH}_4\text{-O}_2$  reaction.

This indicates that the  $\text{SiH}_4\text{-N}_2\text{O}$  combination is considerably more stable than the  $\text{SiH}_4\text{-O}_2$  mixture.

To determine the range of conditions over which the apparent activation energies were applicable, the effect of varying oxidant/ $\text{SiH}_4$  ratio was investigated. To date only preliminary results have been obtained. However, these data indicate that  $\text{O}_2$  has an anomalous effect on the oxidation of  $\text{SiH}_4$  (see Table II). Contrary to expectation, increased oxygen seems to increase the stability of the  $\text{SiH}_4\text{-N}_2\text{-O}_2$  mixture. Conversely, the stability of  $\text{SiH}_4\text{-N}_2\text{-N}_2\text{O}$  mixtures is not affected by increased  $\text{N}_2\text{O}$ .

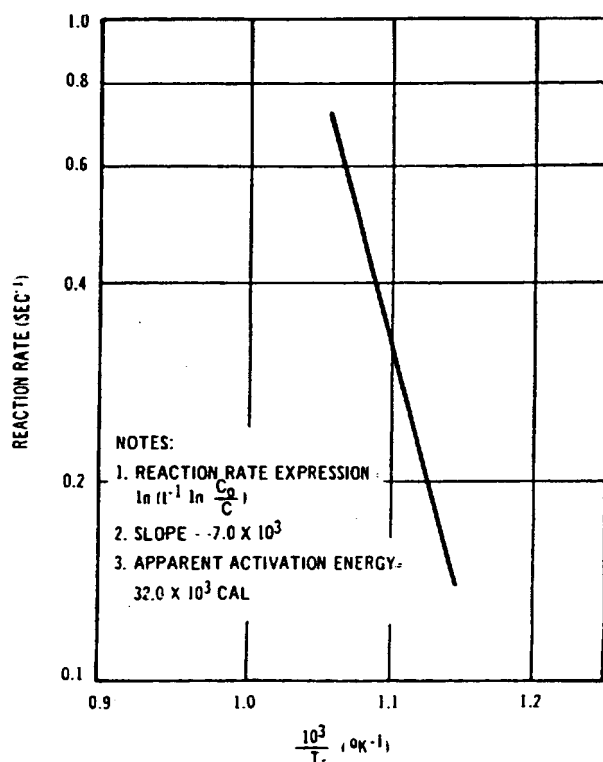
Table II—Initiation Temperatures for Oxidant-SiH<sub>4</sub> Ratios

Oxidant/SiH <sub>4</sub> (Calculated volume ratio based on flow-meter settings)	Initiation Temperature (°C)	
	O <sub>2</sub>	N <sub>2</sub> O
2	139	540
5	197	525
20	257-270	532

In this series of tests, the input SiH<sub>4</sub> concentration was held at 0.4%. The oxidant concentration in all cases was above the stoichiometric concentration. It is most likely that the oxidant was thoroughly mixed with the SiH<sub>4</sub>-N<sub>2</sub> mixture before entering the reactor. Since total flow was held constant (1000 cm<sup>3</sup>/min), no change in reaction temperature was anticipated.

## REACTION PRODUCTS

Further information on the SiH<sub>4</sub> oxidation mechanism was obtained from a materials balance of a partially completed SiH<sub>4</sub>-O<sub>2</sub> reac-

Fig. 8—Temperature dependence of the SiH<sub>4</sub>-N<sub>2</sub>O reaction.

tion. A typical mass spectrographic analysis of a  $\text{SiH}_4\text{-O}_2\text{-N}_2$  mixture before and after reaction is shown in Table III. Analysis of gas mixtures from  $\text{SiH}_4\text{-O}_2$  reactions up to  $450^\circ\text{C}$  similarly indicate that the only gaseous product formed is  $\text{H}_2$ .

These test results indicate that the best overall equation that would describe the  $\text{SiH}_4\text{-O}_2$  reaction at  $240\text{-}450^\circ\text{C}$  for the dilutions employed is



The analytical data for  $\text{H}_2$  in the exhaust stream and  $\text{H}_2$  calculated from the  $\text{SiH}_4$  reaction are in reasonable agreement. On this basis, the absence of  $\text{H}_2\text{O}$  from the exhaust stream can be explained.

Table III—Material Balance (% Concentration by Volume)  
Reaction Temperature— $241^\circ\text{C}$

Gases	Reactor Input	Reactor Exhaust	Reacted	Calculated $\text{H}_2$ , Based on $\text{SiH}_4$ Reacted
$\text{SiH}_4$	0.365	0.124	0.241	—
$\text{O}_2$	0.80 est.	0.575	0.225	—
$\text{H}_2$	—	0.492	—	0.482
$\text{H}_2\text{O}$	—	—	—	—

### CONCLUSIONS

The room-temperature stability of  $\text{SiH}_4\text{-N}_2\text{-O}_2$  mixtures up to 0.8%  $\text{SiH}_4$  indicates that these gases can be premixed well before the deposition reactor. As a result, flow controls at the reactor could be greatly simplified. The use of a single feed stream into a deposition reactor could also simplify the gas-flow pattern within a reactor. This could result in more reproducible deposition results. Further, the sensitivity to leaks in  $\text{SiH}_4$  delivery lines would be reduced by transporting a stable gas mixture from a gas storage area to the reactor.

This study also indicates that  $\text{N}_2\text{O}$  can be used as an oxidant for  $\text{SiH}_4$ . Mixtures of  $\text{SiH}_4\text{-N}_2\text{-N}_2\text{O}$  are considerably more stable and less temperature sensitive than  $\text{SiH}_4\text{-N}_2\text{-O}_2$  mixtures. Thus, the use of  $\text{N}_2\text{O}$  as an oxidant in combination with improved reactor design could lead to a process in which  $\text{SiO}_2$  deposition is essentially confined to wafer surfaces, and phosphorus and boron dopant levels are still accurate and reproducibly controlled.

Another factor of some significance in the study of the  $\text{SiH}_4\text{-O}_2$  reaction is that  $\text{H}_2$  rather than  $\text{H}_2\text{O}$  vapor is formed.

#### ACKNOWLEDGMENTS

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